Chemistry

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1965

SovietRxiv

Abstract

Full Text

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STUDY BY THE E.P.R. METHOD OF FREE RADICALS IN POLYIMIDES

At a temperature of 80-200° water is eliminated from polyamic acids and imide rings are closed (^{1,2}). In the resulting polyimides we detected large amounts of stable free radicals.*

We studied imides of the series:

$$\left[\text{ imide unit containing } R_1 \text{ and } -N-R_2-N- \right]_n$$

in particular, poly(pyromellitimide) (PM):

$$\left[\text{ pyromellitimide residue } -N-\mathrm{C_6H_4}-O-\mathrm{C_6H_4}-N< \right]_n$$

and some of their monomeric analogs.

Radicals of three types were observed. Radicals I (Fig. 1a) (singlet, $\Delta H \sim$ 18-20 oersted) are observed in concentrations up to $n \sim 5 \cdot 10^{17}$ spins/cm^3 in products formed upon heating polyamic acids at 80-200°. An analogous e.p.r. line was found in diaminodiphenyl ether (DADPE) at 130-150°. When the polymers are stored in air, the concentration of radicals I decreases by 10-15% per hour. The shape of the e.p.r. line does not change in this case.

Radicals II (Fig. 1b) (singlet, $\Delta H \sim 6 \div 8$ oersted) are observed in concentrations $n = 10^{17} \div 10^{19}$ spins/cm^3 in polyimides at 200-500°.

In the diimide of pyromellitic acid (DIPK):

$$\text{HN(diimide residue of pyromellitic acid)NH}$$

radicals with an identical e.p.r. spectrum are detected at 200° in concentrations of $5 \cdot 10^{16}$ spins/cm^3, and at 300° of $2 \cdot 10^{18}$ spins/cm^3.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In PM and DIPK at 300° the rates of accumulation of radicals in the initial portions are close (Fig. 3). In polyimides at 20° radicals II decay very slowly, by 10–20% per month, and the shape of the e.p.r. line does not change. High-stability toward hydrolysis and oxidation at 20—300° does not allow the radicals II to be regarded as carbon radicals. By the parameters of the EPR spectrum they are close (3) to the radical:

$$\left[-\mathrm{C_6H_{10}} - \dot{\mathrm{N}} - \mathrm{N} = \mathrm{C_6H_4} =\right]_n$$

In polyimides the radical II is apparently:

$$-\mathrm{R_1} - \mathrm{C(=O)} - \dot{\mathrm{N}} - \mathrm{R_2}-$$

This is partly confirmed by the presence of the same spectrum in DIPK. For DIPK, however, the following variant is possible:

imide ring with the unpaired electron on nitrogen, N·

However, in any case it may be asserted that EPR spectrum II belongs to an unpaired electron localized mainly on the nitrogen atom that is part of the imide ring.

Radical III (Fig. 1, *c*). The characteristic asymmetric shape and large width of the EPR line make it possible to regard radical III as a peroxide radical. In some samples of polyimides it was found together with radicals II at concentrations of $\sim 5 \cdot 10^{18}$ spins/cm^3 at 20°. In the overwhelming majority of samples it could be found at concentrations not exceeding 10^{17} spins/cm^3 at 200°. Upon cooling the polymers, radicals III rapidly disappear.

Fig. 1. Polypyromellitimide (PM). EPR spectra. *a*, *b*, *c* —radicals I, II, III, respectively

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* Scraps of films served as samples. The radicals were detected with an RE 1301 spectrometer. Radical concentrations were calculated by comparison with DPPH standards. The study was carried out in the presence of air.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 2. *a* —heating regime for the initial polyamic acids; *b* —1 —n-concentration of radicals, 2 —EPR linewidth

The kinetics of radical accumulation in PM during stepwise heating of the initial polyamic acid directly in the resonator of the EPR spectrometer* was studied (Fig. 2).

At 80° only radicals I are detected.** After 1 hour of heating at 130° a certain narrowing of the EPR line is observed. At 200°, after expira- or 10 min the evolution of water ceases, the EPR line narrows from 18 to 8 Oe, radicals I disappear, and radicals II begin to accumulate. After the concentration $n \sim 3$—$4 \cdot 10^{17}$ spins/cm^3 is reached, the content of radicals II begins to decrease. Heating to 300° leads to an accelerated accumulation of radicals, after 10-12 min of heating, which is replaced by an accelerated decrease in n. Raising the temperature to 400° gives a burst of concentration up to $\sim 10^{19}$ spins/cm^3. The stationary level: $n \sim 4$—$5 \cdot 10^{18}$ spins/cm^3. When the temperature is lowered, the stationary concentrations of radicals II decrease noticeably, and the level stabilized at 20° depends on the cooling regime.

The presence of reversible and irreversible changes in n is seen from Fig. 4. Raising the temperature by $\sim 40°$ leads to a two- to threefold increase in n, and lowering it leads to the same decrease. There are clearly two irreversible processes: one leads to progressive growth, the other to a decrease in the radical content.

Fig. 3. 1 —temperature, 2 —concentration of radicals II in PM, 3 —concentration of radicals II in DIPK

Fig. 4. 1 —temperature, 2 —concentration of radicals in PM

Their simultaneous development explains the appearance of maxima on the curves $n = n(t)$. In DIPK the second process is absent (Fig. 3).

The identity of the EPR spectra of radicals I and of the radicals formed in DADPE compels one to assume that their structures are identical.

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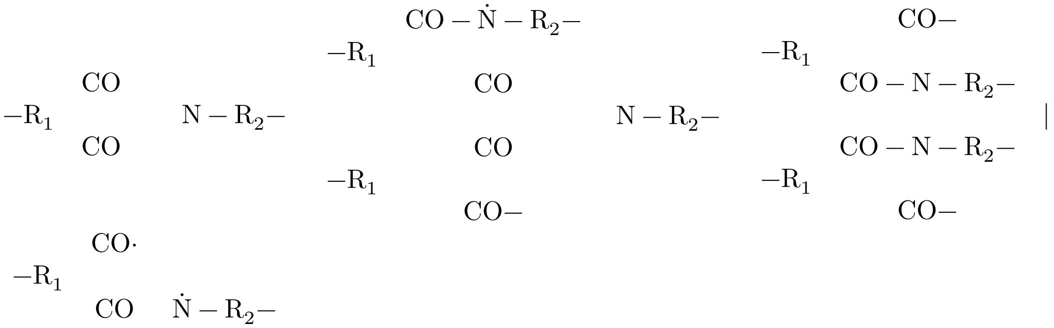
* The time for establishing the temperature in the sample is no more than 1.5 min; the temperature period is $3 \div 5°$.

** Quantitative measurements of the EPR signal intensity at 80—130° are made difficult by the evolution of large amounts of water from the products under study.

The ease of hydrogen abstraction in the amino group of the ether makes it possible to assign to the radical the structure

$$-O- \quad -\dot{N}H$$

In polyamides, radicals I evidently are formed in terminal groups during dehydrogenation of the diamine unit. It is obvious that the formation of radicals I has no direct relation to the principal process in the temperature interval 30—200°—intrachain imidization ([1,2]). If the structure of radical II has been interpreted by us correctly, then the observed changes in the n-concentration of radicals II are associated with opening of imide rings and recombination of the radicals formed.*



$$-R_1\begin{array}{c}CO\\ \\ CO\end{array}N-R_2- \qquad \begin{array}{l} \qquad\quad CO-\dot{N}-R_2- \\ -R_1 \\ \qquad\qquad CO \\ \qquad\qquad\qquad\qquad N-R_2- \\ \qquad\qquad CO \\ -R_1 \\ \qquad\qquad CO- \end{array} \qquad \begin{array}{l} \qquad\qquad CO- \\ -R_1 \\ \qquad CO-N-R_2- \\ \\ \qquad CO-N-R_2- \\ -R_1 \\ \qquad\qquad CO- \end{array} \;\Big|$$

$$\begin{array}{l} \qquad CO\cdot \\ -R_1 \\ \qquad CO \quad \dot{N}-R_2- \end{array}$$

Reversible changes upon a change in temperature (Fig. 3) most likely reflect a shift in the equilibrium of formation and recombination of radicals within one and the same imide rings. The irreversible processes are, most probably, connected with an increasing spatial structur-

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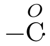
* The reasons for the narrowing of the line of radical II require special consideration.

of polyimides ([2]), as a result of recombination of radicals belonging to different macromolecules. We did not detect radicals to which one could ascribe the structure

$$-\overset{O}{C}\cdot$$

Their apparent absence is possibly explained by the very great width of the EPR line and, accordingly, by the low intensity of the signal in comparison with the signal of radical II. It is possible, however, that the broad lines that disappear with decreasing temperature are due precisely to the high-temperature modification of the radical



$$-\overset{O}{C}\cdot$$

But at low temperatures they undoubtedly belong to the products of their oxidation—peroxide radicals.

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Received
13 III 1965

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Note: Figure translations are in progress. See original paper for figures.